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THE APPLICATION OF NUCLEAR TECHNIQUES TO SOLID STATE DEVICES.(U)
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FINAL TECHNICAL REPORT

submitted to

OFFICE OF NAVAL RESEARCH

on

THE APPLICATION OF NUCLEAR TECHNIQUES
TO SOLID STATE DEVICES.

N00014-75-C-0564

1 January 1975 to 31 August 1980

Principal Investigators

James W. Mayer

Marc-A. Nicolet

December 15, 1980

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I. Introduction

The program "The Application of Nuclear Techniques to Solid State Devices" began on 1 January 1975. It was extended five times on annual intervals and terminated on 31 August 1980. For the Office of Naval Research, the technical monitor of the program was Dr. L. R. Cooper. At the California Institute of Technology, the program was under the scientific direction of Drs. S. S. Lau, J. W. Mayer and M-A. Nicolet. The latter two functioned as the co-principal investigators. Over 70 individuals worked on this project at one time or another, either as regular members of the Caltech research staff, or as occasional collaborators, visitors, students, or staff members. A list of the persons who were involved in the project is given in Section IV.

The project formally pursued two distinct topics: solid-phase epitaxial growth (SPEG) and reaction of thin metal films with silicon substrates. The two topics are treated separately in the following Summary of Scientific Results, (Section II). In fact, however, the two topics were always closely related. Research on both subjects was frequently performed by the same individual, so that ideas and experiments on each topic were constantly intertwined.

Six Ph.D. theses have been completed under the sponsorship of this project. Presently, four of the graduates are working in government laboratories and two have university positions. The contract is acknowledged in some 70 publications in the scientific literature. Abstracts of the theses and a list of

the publications are given at the end of this report (Section V).

It is fair to say that this project was outstandingly successful. The scientific output and the progress accomplished in the 5 1/2 years of its duration are measures of that success. When the project began in 1975, SPEG was a topic that had few followers outside of the group at Caltech and its collaborators. It has now become a popular topic of investigation internationally. The study of silicide reactions by thin films has undergone a similar rise in popularity. And in both instances, the nature of the subject has broadened considerably as a result of this widened attention.

What were the reasons that made this project so successful? In Section III, we attempt to give some answers. Although the analysis given is necessarily based on personal judgement, the effort seemed worthwhile. With this brief analysis, we try to extract one additional useful result from the project. To simply include copies of all publications as is often done for final reports would have produced several volumes of material already in print. To include an analysis of the overall effort, on the other hand, contributes something that none of the published scientific documents does: provide some insight into how a scientific project can succeed.

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II. Summary of Scientific Results

This summary is subdivided into the two topics of solid-phase epitaxial growth (SPEG) and of silicide formation by thin films to reflect the two-pronged nature of the project as it was proposed. In reality, problems and progress in the two topics were always intimately related.

A. Solid-Phase Epitaxial Growth (SPEG)

Investigations supported by a preceding Office of Naval Research (ONR) contract had led to the discovery of the epitaxial growth of amorphous Si and Ge films deposited on a single-crystal substrate covered by a thin transport layer. Elemental metal layers and a Pd_2Si film were known to act as transport media. Our studies followed two distinct avenues of investigations for these two transport media.

For Pd_2Si as a transport medium we determined initially that it was possible to dope the regrown layer by adding a dopant species such as Sb (1)*. We also developed a radioactive tracer technique based on the activation of ^{30}Si by thermal neutrons in a reactor and were then able to demonstrate that the epitaxial growth proceeds by a precipitation of the Si incorporated in the silicide which is itself replaced by Si from the overlying amorphous Si layer (8, 15, 35)*. Detailed investigations had shown previously that on a (100) surface the precipitation begins by nucleation of islands which subsequently extend laterally and coalesce to a layer whose thickness is given by that of the initial Pd_2Si transport layer (16)*. We

* Refer to running numbers in the Section listing publications.

discovered that the process is a repetitive one, each individual layer growing less rapidly than the previous one (13)*. Transmission electron micrographs of the grown layer showed that twinning occurred at each new stage of nucleation and that Pd-containing inclusion were present as well (17)*. At times, reproducibility was a serious difficulty in these experiments. The problem was ultimately traced to impurities incorporated in the amorphous Si layer during the vacuum deposition, and carbon being a major constituent (18)*. We also established that Pd_2Si was not a unique case, but that silicides of Ni, Pd, Pt, Co, Fe, Cr, V, Ti or Rh all can mediate SPEG of amorphous Si layers. The temperature at which SPEG proceeds at a given rate correlates with the heat of formation of the silicide, its melting point and its formation temperature (19)*. On Si (111) substrates, the epigrowth of Si can take place on top of a Pd_2Si film because this silicide forms epitaxially on (111) Si substrates. The result is a hetero-epitaxial structure of $\text{Si}(111)/\text{Pd}_2\text{Si}/\text{Si}$ (14)*.

For elemental metal layers as transport medium, the process was found not to be a matter of volume solubility of Si (or Ge) in the metal, but rather a question of diffusivity through extended defects, because eutectic-forming metals such as Al, Ag and Au all exhibited the phenomenon, and the solubility of Si changes by orders of magnitudes in these elements. These studies led to the realization that thin polycrystalline Si films covered by an Al (or Au) layer, as is frequently the case in MOS devices, were unstable insofar as the metal film provided a medium in which the fine-grained polycrystalline Si could recrystallize in form of larger grains imbedded in the metal (3)*.

Our investigations on SPEG convinced us that it should be possible to grow epitaxially amorphous Si layers on Si single-crystal substrates without interposed transport layer. Attempts to accomplish this with vacuum-deposited layers failed. We therefore resorted to the implantation of Si into Si single-crystal substrate at sufficiently high doses to amorphize a surface layer completely. Upon thermal annealing, these layers were shown to regrow epitaxially at absolute temperatures near half that of the melting point of Si (7)*. Impurities and imperfections in the amorphous layer and at the layer-substrate interface were evidently minimized sufficiently so as not to interfere with the SPEG process. This approach turned out to be most fruitful and rapidly yielded much detailed information on SPEG amorphous Si. We found that the growth rate was linear in time for all substrate orientations, except close to (111), but that the rate varied with the orientation. A simple model assuming lateral growth along (111) planes was able to explain most facts (12)*. Amorphous Ge layers prepared in analogous fashion on single crystalline Ge substrates exhibited a very similar behavior (11)*. By implantation of impurities into the amorphized Si layer, ^{16}O , ^{12}C and ^{14}N were found to appreciably retard the growth at levels of about 0.5 at. % (10)*, while ^{11}B , ^{31}P and ^{75}As enhance the growth very substantially (9)*. Noble gases, on the other hand, interfere with the growth process by their tendency to form microbubbles which seem to be effective nucleation sites for microtwins (25, 26)*. Sputtered Si layers deposited on single crystalline Si substrates were shown not to regrow epitaxially because the residual concentration of the sputtering gas in the film

exceeds the maximum allowable value admissible for SPEG to take place (28)*. The state of our understanding of SPEG of Si and Ge by thermal annealing was summarized in several reviews (24, 38, 42)*.

Transient annealing was then introduced as an alternative to steady-state furnace annealing of amorphized Si layers and it was found that epitaxial regrowth could be achieved by a Q-switched ruby laser pulse (30)*. The main observations could be explained by a model based on melting of the amorphous layer and subsequent epitaxial recrystallization. Soon thereafter, we also succeeded in inducing epitaxial growth of deposited amorphous Si layers on (100) Si single-crystal substrates by a Q-switched Nd-YAG laser (32)*. The interfacial oxide obstacle which usually leads to polycrystalline formation in furnace annealing of deposited layers was thus overcome by pulsed annealing. We were also able to achieve heteroepitaxial growth of deposited amorphous Ge layers on (100) and (111) Si single-crystal substrates by a pulsed electron beam (33)*. The primary defects observed in the (100) case were dislocations, whereas stacking faults were observed in the (111) samples. The same heteroepitaxial growth was also achieved by a Q-switched Nd-YAG laser and with very similar results (47)*. Pulsed electron beams were also shown to induce epitaxial regrowth of ion-implanted amorphous Si layers on (100) and (111) Si substrates (49)*, as well as the doping of Si by deposited thin Si films (58)*. All these transient annealing experiments were consistent with the idea that the energy of the (electron or laser) pulse simply melted the surface layer and that the subsequent epitaxial growth was the consequence of a rapid solidification of the layer. The speed of progression of the regrowth front is then deter-

mined by the rate of heat loss into the substrate. It was established, however, that the initial depth of the melted layer depends strongly on the amount of damage in the implanted layer, because the heat of fusion of a fully amorphized layer is about 5 kcal/mole below that of single crystalline Si (12 kcal/mole) (49)*. A comparative study of pulsed laser and electron beam annealing of deposited amorphous Ge and Si layers on (100) and (111) Si single-crystal substrates concluded that electron beams may be more generally applicable because the heat generated is less material dependent and more uniform in depth than with lasers, and there is less reflection of incident energy (52)*. The crystallization of implanted amorphous Si layers by laser and furnace annealing has also been compared (50)*. For Q-switched lasers, there is an energy threshold for epitaxial growth that corresponds to the melting of the whole amorphous layer. Supersaturation or segregation of impurities is observed as a result of the fast melt-quenched regrowth process (51)*. For scanned cw lasers, solid-phase regrowth can occur at temperatures below the melting point of Si. The lack of redistribution of impurities and the dependence of the crystalline quality on the substrate orientation are similar to the features observed for SPEG in furnace-annealed samples. Regrowth of Te-implanted GaAs by Q-switched ruby laser irradiation was also successfully demonstrated (59)*. In general, the GaAs results were consistent with the melting model used to describe the results for Si and Ge.

It was during the course of these experiments on transient annealing that we came upon the fact that amorphous Si films vacuum-deposited on Si single-crystal substrate could regrow epitaxially

also upon steady-state annealing, using conventional chemical cleaning procedures and a standard dry-pumped vacuum system (53)*. The stage of detectable epigrowth is preceded by a delay period which is attributed to the reduced growth rate of a contaminated interfacial layer. Regrowth was accomplished even with a simple solar concentrator as the heat source (56, 65)*. SPEG of deposited Si layers under steady-state annealing conditions was shown to proceed by island growth. The main residual impurities in our cleaning process are carbon and oxygen (69, 76)*. Another critical factor is the rate of deposition of the amorphous Si layer. Fast depositions ($\sim 50 \text{ \AA/sec}$) on Si substrates dipped into a diluted HF bath immediately before loading in the vacuum system leads to a layer-by-layer growth similar to that found in self-ion implanted amorphous layers, and with similar growth rates; but slow ($\sim 2 \text{ \AA/sec}$) depositions result in much reduced regrowth rates (76)* because such films are porous. A general review of epitaxial growth by thermal, laser and electron beam annealing has been written (73)*.

B. Silicide Formation by Thin Films

The formation of silicide layers by the reaction of thin metal films deposited on silicon substrates had been investigated over the last five years preceding this contract, both by our group and by others. The behavior of a number of silicide-forming transition metals upon thermal annealing had been well characterized phenomenologically. Our efforts therefore addressed themselves toward broadening the basis of experimental facts and deepening the understanding of thin-film reactions.

Germanium substrates were introduced as alternatives to Si to broaden the scope. We found that the first nucleating phase agreed with the prediction of the Walser-Bené rule for all elements tested (Co, Hf, Ni, Pd, and Rh) except Pd (5)*. In that case, Pd₂Ge grows first and PdGe comes second, rather than first. Both these phases were found to grow with a (time)^{1/2} dependence. The activation energy is the same for both reactions (1.5 ± 0.1 eV), and the reactions are about three times faster on amorphous substrates than on single crystalline Ge (39)*.

Significant new insight was derived from radioactive ³¹Si tracer experiments. We confirmed that Ni is the moving specie in the formation of Ni₂Si, and concluded that the diffusion is via grain boundaries (20)*. Pt is also the diffusing specie in Pt₂Si formation, but both Pd and Si are moving when Pd₂Si forms (35)*, as the same technique showed. We then applied the method to clarify the atomic transport in bimetal layer silicide reactions. In these experiments, two films of different metals are deposited sequentially on Si, rather than one. The initial study with ³¹Si was performed for Cr films on Pd. Upon thermal annealing, a uniform film of Pd₂Si is formed initially, followed by the subsequent growth of a CrSi₂ layer on top of the Pd₂Si film. The Si atoms in the CrSi₂ layer came partly from the Pd₂Si layer, and partly from the Si substrate. At high temperatures, the ratio of these two contributions can be readily interpreted as resulting from a rapid self diffusion of the Si within both silicides as compared to the rate of CrSi₂ growth (21, 35)*. Similar results were obtained for Cr films on Pt films

on Si (21)*. The oxidation of Si, CoSi_2 and PtSi was also investigated by the same marker method (54)*. On both Si and the silicides, the SiO_2 grows by diffusion of oxygen through the SiO_2 to the interface, where the additional SiO_2 is formed. In the silicide case, the silicon reacting with the oxygen at the interface originates from both the substrate and from the silicide layer in a ratio that is controlled by the fact that the self diffusion of Si across the silicide is rapid compared to the rate of SiO_2 growth. We also succeeded in establishing how the second silicide phase NiSi forms from the first phase Ni_2Si because of a fortuitous accumulation of a heavy atom (Pt) at the $\text{Ni}_2\text{Si}/\text{Si}$ interface that acts as a marker in the transformation (23)*. NiSi grows by the decomposition of Ni_2Si at the $\text{NiSi}/\text{Ni}_2\text{Si}$ interface and the simplest assumption is that the Ni diffuses through the NiSi to form additional NiSi at the substrate NiSi interface.

Compared to the late transition metals Ni, Pd and Pt, the silicide reactions of early transition metal (e.g., Ti, Zr, V, Nb) are poorly characterized and understood. We spent considerable effort trying to elucidate the problems associated with these metals. We found both $(\text{time})^{1/2}$ and $(\text{time})^1$ dependent growths. We could not find a simple correlation of contaminant level with growth rate reduction. We always found the same disilicide phase, though. The question of the true growth rate of these silicides remains open (27)*. Cobalt silicide formation was also investigated. There, too, anomalies were found in that both Co_2Si and CoSi grow simultaneously in discrete layers (22)*. There, too, the root cause for this anomaly has yet to be identified. The effect of stress on silicide reaction was also

found to be difficult to measure and assess (63)*.

Bimetal film experiments were also conducted. For all three binary combinations of the near-noble metals Ni, Pd and Pt (78, 37, 48)*. A uniform film of a ternary monosilicide composition results upon annealing at about 700°C. Below 600°C, the layers are highly nonhomogeneous in depth. The formation of a homogeneous ternary layer is not surprising since all the monosilicides of these elements have the same orthorhombic crystal structure. The bimetal silicides are all of different structure, which explains why the low-temperature phases do not form a homogeneous layer. As a contrast, we also studied Pd/V bilayers (48)*. The silicides observed in thin-film reactions of these elements taken individually all have different crystal structure and the silicide reactions of these two elements behave generally in different fashion. Not surprisingly, we found that after annealing, the two metals form spatially segregated silicides. When Pd is on the bottom, the two silicides are uniform and retain the original metal sequence. In the other case, the sequence is inverted, but lateral nonuniformities remain. A review summarizing our and others work on silicide formation has been written (75)*.

Toward the end of the project, we devoted increasing attention to the nature and role of the silicide-Si interface. Using the UHV deposition system equipped with in situ BS, AUGER and substrate temperature control at Bell Labs, as well as channeling measurements in the backscattering and the transmission mode, the Ni-Si (111) interface was shown to contain on the order of 1×10^{16} atoms/cm² of nonregistered Si for thick ($> 10^{16}$ Ni/cm²) Ni layers (74)*.

The actual number depends on the Ni coverage, the deposition temperature, and the subsequent temperature/time cycle. The results stress the role of the kinetics in establishing the actual characteristics of a metal-Si interface. An XPS study of that interface showed that chemically the interface is a graded region with composition varying from Si-rich to Ni-rich over a distance of about $10\text{--}20 \text{ \AA}$ (72)*. Similar results apply for the interfaces between Ni and Ni_2Si , and Ni_2Si and Si. In another study, the epitaxially growing phase NiSi_2 has been shown to have properties that can be explained from the nucleation-controlled morphology of the silicide-Si interface (61)*. We also explained the anomalously high thermal stability of Pd_2Si on Si substrates and the observed decomposition of PdSi into $\text{Pd}_2\text{Si} + \text{Si}$ when in contact with Si (which is contrary to the equilibrium phase diagram) as a result of the very low interfacial energy of the (highly coherent) Pd_2Si -Si interface (68)*.

A natural outgrowth of these investigations of silicide formation was the question how these reactions could be suppressed. The problem was researched (36)* and led to independently sponsored studies on thin-film diffusion barriers based on refractory metal compounds.

In addition to conventional thermal annealing, we have also applied directed energy in form of ion-, electron- and laser-beams to induce reactions between thin metal films and Si substrates. Of this work, that on ion-beam-mixing was later supported independently. It started, however, under this project with experiments on silicide

formation by high-dose Si ion irradiation of Pd films (46)* and by noble gas ion irradiation of Ni, Pt and Hf films on Si substrates (45)*. These experiments established or confirmed essential statements on ion-beam-mixing, viz. (dose)^{1/2} dependence; silicide formation; independence on ion species; dependence on irradiation temperature.

Pulsed laser annealing to achieve solid-phase thin-film reactions has been investigated analytically (44)* and experimentally on a number of systems. Even pn junctions formed by laser-pulse annealing of Sb films on Si have been investigated (67, 64)*. It was rapidly recognized that on pure Si substrates the unlimited supply of Si led to uncontrollable morphologies and the coexistence of a number of phases (60)*. The weak coupling of metals with lasers also creates difficulties. These problems were most profitably resolved by studying bilayers or multilayered films on inert substrates. With this approach, the overall composition is predetermined and fixed. We succeeded in producing metastable amorphous phases of Pt-Si and Pd-Si this way over all compositions except those close to the congruently melting phases and the pure elements (62)*. Thermal decomposition of Si-rich amorphous films revealed the formation of at least two metastable crystalline phases in the Pt-Si system, and a low-temperature nucleation of the PdSi phase in the Pd-Si case. Corresponding experiments with Au-Si gave amorphous phases from 9 to 91 at. % Au and a single metastable hexagonal phase upon thermal decomposition between 50 and 80°C (55)*. A review comparing laser- and ion-beam-induced reactions summarizes these results (71)*.

III. Retrospective and Outlook

The most singly significant reason for the success of the project was that it was based on two sound ideas at the start. The existence of SPEG had been established previously by MeV He channeling experiments during work sponsored by ONR in a preceding contract (N000-14-67-A-0094-0035). Similarly, we had shown at Caltech under the same previous ONR sponsorship that thin-film reactions of metal films with silicon substrates could be investigated quantitatively by MeV He backscattering spectrometry. These were both *topics of potentially high practical relevance* and they ultimately attracted wide attention because of that. They were also *topics ready for successful attack*. The main tool of investigation - backscattering spectrometry and channeling - had just been developed for routine analytical application. The group at Caltech possessed the technique and knew its possibilities and limitations. Largely because of the novelty of applying these analytical methods to solid-state studies, these *topics were leading into largely virgin territory*. This combination of relevance, timeliness, and novelty constituted a favorable starting point.

In order to realize success from that auspicious initial position, some additional elements had to be brought together. Foremost among these were people and attitudes. The Office of Naval Research committed itself to *long-term support of the project at a continuous level*; it gave the researchers *great flexibility of action* at a minimum of contractual requirements, and it established *close personal contact between the contract monitors and the investi-*

gators instead. At the California Institute of Technology, the three main investigators offered *dedicated leadership* that managed to attract qualified researchers and students and form a group of action.

The beneficial effect of a long-term support at a steady and appropriate level is that it permits planning beyond the usual 12-month horizon of contractual support. The project supported Dr. S. S. Lau on a full-time basis for years. In return, Dr. Lau added leadership and continuity to the group, on matters of SPEG in particular. The project also benefitted from the services of a full-time technician, Rob Gorris, who became an invaluable source of assistance and know-how in matters of designing, building and maintaining instruments and set-ups. His presence had much to do with the rapidity with which the group could respond to new ideas with new experiments. Finally, the project provided support for about one additional visitor and general expenses.

The ability to pursue ideas at once when they spring up has been a key factor in the success of the project. Just as importantly, the group also enjoyed the liberty to act, even though an experiment may not have been anticipated in a proposal. There have been a number of instances in the course of this project where major progress resulted from such unanticipated developments. In 1976 we developed, on an unscheduled basis, a marker technique based on radioactive ^{31}Si with Dr. R. Pretorius, who happened to have a good background in nuclear chemistry. The method provided the most detailed information available yet on atomic transport in SPEG as well as in thin-film silicide reactions. The method now constitutes

Dr. Pretorius' main line of research in South Africa. In 1978 transient annealing by lasers and electron beams was similarly introduced in improvised fashion as an alternative to the steady-state annealing step used until then both for SPEG and thin-film reactions. It was as the direct result of these unforeseen experiments that SPEG of amorphous deposited Si layers on single crystalline substrates became a reality in 1979 for steady-state furnace annealing as well, using only conventional vacuum deposition and chemical cleaning procedures. The subjects of epitaxial growth of deposited layers (both homo- and hetero- epitaxial) by steady-state and by transient annealing are now drawing much interest and support internationally. The hope is that these processes may lead to improved or novel devices or processing methods for integrated circuits and solar cells. Other topics that were included into the project as a result of a passing opportunity were the gettering of Au in Si single-crystal wafers by pairing with P impurity atoms and by dislocation networks, the anodic oxidation of InP single crystals, thermal annealing experiments by solar collectors, and others.

Flexibility also spawned research projects that went their own distinct routes. The insights we gained from our regrowth experiments of Si-implanted amorphous layers on Si single-crystal substrates lead quite naturally to similar experiments on Si-on-Sapphire (SOS) (57, 66)* and on GaAs (59)*. The improvement of the crystalline quality of SOS by Si implantation and subsequent regrowth has since been investigated to a large degree in industrial labora-

tories. In another spin-off, the regrowth of amorphized GaAs layers has been pursued at Caltech under separate sponsorship. Finally, the studies of thin-film silicide reaction lead to the inverse question how these reactions could be prevented. Out of that question arose an independent program on diffusion barriers in which the group took a leading role.

A comparison of the annual proposals of the project and the subsequent accomplishments listed in the following year leads to the interesting observation that *the full execution of an idea typically lagged 2 or 3 years behind its first formulation in an annual proposal*. Noticeable exceptions are experiments that were initiated on an unscheduled basis (such as the radioactive tracer experiments, or the transient annealing experiments). The impact of these experiments on the regularly scheduled work was rapid, and long-lasting in the sense that they redirected the subsequent course of research and of our thinking. They also lead to an accelerated rate of progress. The clearest example is the successful execution of SPEG of deposited amorphous layers by furnace annealing: it occurred as a result of having introduced transient annealing as an (unscheduled) alternative to steady-state annealing. The lesson is that *providing room for an unexpected fruitful idea should be a guiding concept in conducting, monitoring and administering research projects*.

The time interval of 2 to 3 years from the first proposal to the full execution is surprisingly long. But the reasons are relatively simple to enumerate. When proposed, an idea is, at best, known to be promising from preliminary experiments. The first year

is spent in performing a conclusive experiment. In the process, more is learned about the topic. A comprehensive approach is then laid out and corresponding experimental improvements are performed. If a two-year time span for the execution of a project is thus considered as reasonable minimum, it follows that *the typical one-year period for contract support is not an optimal procedure for research of this kind.*

While some projects were added on an unscheduled basis, others that had been proposed were never executed. For example, the first proposal of 1975 anticipated an investigation of the reaction of thin Si films deposited on metal substrates. This complementary version of the usual metal-film-on-silicon experiment has now recently been performed by other investigators. Other experiments that are still awaiting execution are, for example, to test the role of impurities in SPEG of Ge; to test if the role of impurities on the regrowth of amorphized Si layers on Si single-crystal substrates depends on the sequence of the amorphizing Si implantation and the impurity implantation.

It is the mark of a dynamic field of investigation that success also multiplies the number of new and fruitful lines of research. The success of this project can also be evaluated from that perspective. In 1976, the proposal anticipated experiments of ion implantation "to modify the metal-Si (or Ge) interface at various stages of the compound formation". This idea forms the basis of what later became known as ion-beam mixing, or stitching, and has grown into a discipline of its own. At Caltech, it was sponsored independently first by the Office of Naval Research, and

later by the Joint Services Electronics Program. Characteristically, it was only by 1979 - three years after the proposal was made - that the topic could be investigated with vigor and then began to develop rapidly as a result of the work performed at Caltech.

Another outgrowth of promise is visible in the experiments combining electrical measurements with those of SPEG. Results indicate that nucleation processes can be monitored sensitively by such measurements under suitable conditions. This idea shows similarity with that of SPEG that was at the starting point of the project now coming to a close. The strength of that project resided in its combination of appropriate tools with pertinent ideas. In particular, the combination of ion implantation (as ion irradiation) with high-purity single-crystal substrate materials offered an approach where the highly reproducible conditions necessary for successful experiments with SPEG could be realized readily. To combine these same attributes for a concerted effort on studies of nucleation is an appealing idea. By adding electrical measurements, SPEG studies also would be brought one step closer to their practically useful application in electronic devices.

Why did this highly successful project come to an end? The visible cause is the breakup of the leading group in Summer 1980. J. W. Mayer took a position at Cornell University and S. S. Lau went to the University of California at San Diego. They left because these institutions offered them professional opportunities they considered superior to those existing at the California Institute of Technology. The termination of the project as it existed is thus the

result of Caltech's inability to retain these individuals, and not of ONR's doing. Possibly it was the remarkable accomplishments of the project that lead to this turn of events. The desire of other institutions to have a part in that successful activity outweighed Caltech's determination to retain it.

To ONR, the new situation poses new problems. Should work in this field continue in only one, or two, of the three institutions now represented? For the immediate, the answer has been only Cornell. But the existence of three individual groups instead of a single one could turn out to be to the long-range advantage of the progress in the field. To that end, a coordinated research activity in the three groups and a balanced supporting strategy should exist. ONR's funding decisions will have a significant influence on the future of the field and that of the three groups. The transition period during which each of these groups must now seek particular areas of activity is of particular significance. It is hoped that this report will assist ONR in defining its options and formulating decisions.

IV. Scientific Collaborators

The following were engaged in research under project
N00014-75-C-0564 at the California Institute of Technology:

<u>Investigator</u>	<u>Status</u>	<u>Present Address</u>
J. E. Baker	Collaborator	University of Illinois, Urbana-Champaign
S. U. Campisano	Collaborator	Istituto Di Struttura di Materia, Catania, Italy
C. Canali	Collaborator	Istituto Di Fiscia, Modena, Italy
G. E. Chapman	Research Fellow	Riverina College of Advanced Education, Wagga Wagga, Australia
N. W. Cheung	Student and Research Fellow	University of California Berkeley, California
L. Csepregi	Research Fellow	Institut für Festkör- pertechnologie, München, West Germany
R. J. Culbertson	Collaborator	Bell Labs, Murray Hill, New Jersey
R. C. Eckardt	Collaborator	Naval Research Lab, Washington, D. C.
F. H. Eisen	Collaborator	Rockwell International Science Center, Thousand Oaks, California
L. C. Feldman	Collaborator	Bell Labs, Murray Hill, New Jersey
R. Fernandez	Technician	Caltech
G. Ferrari	Collaborator	Istituto Di Fisica, Modena, Italy
R. Ferrari	Collaborator	Istituto Di Fisica, Modena, Italy
T. Finstad	Research Fellow	University of Oslo, Oslo, Norway

Scientific Collaborators (continued)

G. Foti	Collaborator	Istituto Di Struttura di Materia, Catania, Italy
J. F. Gibbons	Collaborator	Stanford University, Stanford, California
I. Golecki	Research Fellow and Visiting Associate	Rockwell International, Anaheim, California
R. Gorris	Technician	Caltech
F. J. Grunthaner	Collaborator	Jet Propulsion Lab, Pasadena, California
P. J. Grunthaner	Student	Jet Propulsion Lab, Pasadena, California
J. Gyulai	Visiting Associate	Central Research Institute for Physics, Budapest, Hungary
J. M. Harris	Student and Collaborator	Sandia Laboratories, Albuquerque, New Mexico
L. S. Hung	Research Fellow	Cornell University Ithaca, New York
E. F. Kennedy	Visiting Associate	College of the Holy Cross, Worcester, Massachusetts
A. R. Kirkpatrick	Collaborator	SPIRE Corporation, Bedford, Massachusetts
T. Koji	Research Fellow	Kochi-ken, 781-34, Japan
S. S. Lau	Senior Research Fellow	University of California at San Diego, La Jolla, California
Z. L. Liau	Student	Lincoln Laboratory, Lexington, Massachusetts
D. L. Lile	Collaborator	Naval Ocean Systems Center, San Diego, California

Scientific Collaborators (continued)

M. Mäenpää	Research Fellow	Caltech
G. Majni	Collaborator	Istituto Di Fisica, Modena, Italy
J. Mallory	Technician	-
S. Matteson	Research Fellow	Texas Instruments, Inc., Dallas, Texas
J. W. Mayer	Professor	Cornell University, Ithaca, New York
J. Minnucci	Collaborator	SPIRE Corporation, Bedford, Massachusetts
K. Nakamura	Research Fellow	Nippon Electric Co., Ltd. Kawasaki, Japan
M-A. Nicolet	Professor	Caltech
C. Norris	Secretary	-
J. O. Olowolafe	Student and Collaborator	University of Ife, Ile-Ife, Nigeria
G. Ottaviani	Collaborator	Istituto Di Fisica, Modena, Italy
M. Parks	Secretary	Caltech
R. Pretorius	Research Fellow	Southern Universities Nuclear Institute, Faure, South Africa
M. Prudenziati	Collaborator	Istituto Di Fisica, Modena, Italy
C. L. Ramiller	Student	Intel Magnetics, Santa Clara, California
J. L. Regolini	Collaborator	Stanford University, Stanford, California
P. Revesz	Research Fellow	Central Research Institute for Physics, Budapest, Hungary

Scientific Collaborators (continued)

E. Rimini	Collaborator	Istituto Di Struttura di Materia, Catania, Italy
J. Roth	Research Fellow	Max-Planck-Institut für Plasmaphysik, Garching bei München, West Germany
J. A. Roth	Collaborator	Hughes Research Lab, Malibu, California
M. Roulet	Collaborator	Centre Electronique Horloger, Neuchatel, Switzerland
D. K. Sadana	Collaborator	Lawrence Berkeley Lab, Berkeley, California
P. Schwob	Collaborator	Centre Electronique Horloger, Neuchatel, Switzerland
T. E. Seidel	Research Fellow	Bell Laboratories, Murray Hill, New Jersey
T. T. Sheng	Collaborator	Bell Laboratories, Murray Hill, New Jersey
T. W. Sigmon	Visiting Associate	Stanford University, Stanford, California
P. J. Silverman	Collaborator	Bell Laboratories, Murray Hill, New Jersey
W. Strydom	Collaborator	Southern Universities Nuclear Institute, Faure, South Africa
T. Sugannma	Collaborator	Nippon Electric Co., Ltd. Kawasaki, Japan
J. L. Tandon	Research Fellow	Royal Melbourne Institute of Technology, Melbourne Australia
D. Tonn	Technician	University of Arizona, Tempe, Arizona
B. Y. Tsaur	Student	Lincoln Laboratory, Lexington, Massachusetts

Scientific Collaborators (continued)

W. F. Tseng	Research Fellow	Naval Research Lab, Washington, D. C.
K. N. Tu	Collaborator	IBM, Research Center, Yorktown Heights, New York
M. von Allmen	Visiting Associate	University of Bern, Bern, Switzerland
H. von Seefeld	Research Fellow	Max-Planck-Institut für Plasmaphysik, Garching bei München, West Germany
N. K. Wagner	Collaborator	Naval Ocean Systems Center, San Diego, California
R. Wagner	Research Fellow	Naval Research Lab, Washington, D. C.
K. W. West	Collaborator	Bell Laboratories, Murray Hill, New Jersey
P. Williams	Collaborator	University of Illinois, Urbana-Champaign, Ill.
M. Wittmer	Research Fellow	BBC Brown Boveri & Co., Baden, Switzerland

V. Scientific Writings

The following documents acknowledge support by the Office of Naval Research under project N00014-75-C-0564.

A. Theses:

1. PART I ENERGY STRAGGLING OF ^4He BELOW 2.0 MeV IN Al,
Ni, Au AND Pt

PART II STUDIES OF THE Ti-W METALLIZATION SYSTEM ON SI

by

Joe M. Harris

California Institute of Technology

July, 1975

PART I

In recent years, backscattering spectrometry has become an important tool for the analysis of thin films. An inherent limitation, though, is the loss of depth resolution due to energy straggling of the beam. To investigate this, energy straggling of ^4He has been measured in thin films of Ni, Al, Au and Pt. Straggling is roughly proportional to square root of thickness, appears to have a slight energy dependence and generally decreases with decreasing atomic number of the adsorber. The results are compared with predictions of theory and with previous measurements. While Ni measurements are in fair agreement with Bohr's theory, Al measurements are 30% above and Au measurements are 40% below predicted values. The Au and Pt measurements give straggling values which are close to one another.

PART II

MeV backscattering spectrometry and X-ray diffraction are used to investigate the behavior of sputter-deposited Ti-W mixed films on Si substrates. During vacuum anneals at temperatures near 700°C for several hours, the metallization layer reacts with the substrate. Backscattering analysis shows that the resulting compound layer is uniform in composition and contains Ti, W and Si. The Ti:W ratio in the compound corresponds to that of the deposited metal film. X-ray analyses with Reed and Guinier cameras reveal the presence of the ternary $\text{Ti}_x\text{W}_{(1-x)}\text{Si}_2$ compound. Its composition is unaffected by oxygen contamination during annealing, but the reaction rate is affected. The rate measured on samples with about 15% oxygen contamination after annealing is linear, of the order of 0.5 Å per second at 725°C, and depends on the crystallographic orientation of the substrate and the dc bias during sputter-deposition of the Ti-W film.

Au layers of about 1000 Å thickness were deposited onto unreacted Ti-W films on Si. When annealed at 400°C these samples underwent a color change, and SEM micrographs of the samples showed that an intricate pattern of fissures which were typically 3µm wide had evolved. Analysis by electron microprobe revealed that Au had segregated preferentially into the fissures. This result suggests that Ti-W is not a barrier to Au-Si intermixing at 400°C.

2. SILICIDE FORMATION AND THE INTERACTION OF METALS
WITH POLYCRYSTALLINE SI

by
Johnson Olufemi Olowolafe

California Institute of Technology

January, 1977

The main factors affecting solid-phase Si-metal interactions are reported in this work. The influence of the orientation of the Si substrates and the presence of impurities in metal films and at the Si-metal interface on the formation of nickel and chromium silicides have been demonstrated. We have observed that the formation and kinetic rate of growth of nickel silicides is strongly dependent on the orientation and crystallinity of the Si substrates; a fact which, up to date, has never been seriously investigated in silicide formation. Impurity contaminations in the Cr film and at the Si-Cr interface are the most dominant influencing factors in the formation and kinetic rate of growth of CrSi_2 . The potentiality and use of silicides as a diffusion barrier in metallization on silicon devices were also investigated.

Two phases, Ni_2Si and NiSi , form simultaneously in two distinct sublayers in the reaction of Ni with amorphous Si, while only the former phase was observed on other substrates. On $\langle 111 \rangle$ oriented Si substrates the growth rate is about 2 to 3 times less than that on $\langle 100 \rangle$ or polycrystalline Si. Transmission electron micrographs establish that silicide layers grown on different substrates have different microcrystalline structures. The concept of grain-boundary diffusion is speculated to be an important factor in silicide formation.

The composition and kinetic rate of CrSi_2 formation are not influenced by the underlying Si substrate. While the orientation of the Si substrate does not affect the formation of CrSi_2 , the purity of the Cr film and the state of Si-Cr interface become the predominant factors in the reaction process. With an interposed layer of Pd_2Si between the Cr film and the Si substrate, CrSi_2 starts to form at a much lower temperature (400°C) relative to the Si-Cr system. However, the growth rate of CrSi_2 is observed to be independent of the thickness of the Pd_2Si layer. For both Si-Cr and Si- Pd_2Si -Cr samples, the growth rate is linear with time with an activation energy of 1.7 ± 0.1 eV.

A tracer technique using radioactive ^{31}Si ($T_{1/2} = 2.26$ h) was used to study the formation of CrSi_2 on Pd_2Si . It is established from this experiment that the growth of CrSi_2 takes place partly by transport of Si directly from the Si substrate and partly by breaking Pd_2Si bonds, making free Si atoms available for the growth process.

The role of CrSi_2 in Pd-Al metallization on Si was studied. It is established that a thin CrSi_2 layer can be used as a diffusion barrier to prevent Al from interacting with Pd_2Si in the Pd-Al metallization on Si.

As a generalization of what has been observed for polycrystalline-Si-Al interaction, the reactions between polycrystalline Si (poly Si) and other metals were studied. The metals investigated include Ni, Cr, Pd, Ag and Au. For Ni, Cr and Pd, annealing results in silicide formation, at temperatures similar to those observed on single crystal Si substrates. For Al, Ag and Au, which form simple

eutectics with Si annealing results in erosion of the poly Si layer and growth of Si crystallites in the metal films.

Backscattering spectrometry with 2.0 and 2.3 MeV ^4He ions was the main analytical tool used in all our investigations. Other experimental techniques include the Read camera glancing angle x-ray diffraction, scanning electron, optical and transmission electron microscopy.

3. ION BOMBARDMENT EFFECTS ON MATERIAL COMPOSITIONS

- PREFERENTIAL SPUTTERING AND ATOMIC MIXING

by

Zong-Long Liao

California Institute of Technology

November, 1978

This thesis reports a study of the effects of ion bombardment on material composition and their implications in material modification and analysis. First, composition changes in binary alloys and compounds as a result of rare-gas sputtering were observed by using Rutherford backscattering techniques. The heavier components were generally found to become enriched in a surface layer whose thickness corresponded to the ion range. After an amount of material comparable to this thickness had been sputter-removed, the surface layer reached a steady-state. The steady-state surface composition was independent of the mass and energy of the sputtering ion. (Chapters 2 and 3)

The results were interpreted in terms of a preferential sputtering, which generated enrichment of the heavy species at

surface, in combination with an ion-induced atomic mixing effect, which propagated the composition change over a depth comparable to the ion range. A model based on this interpretation seemed to combine all experimental results into a consistent picture.

(Chapter 4)

The model was then extended to study the phenomena of high-dose ion implantation. The idea of preferential sputtering was used to predict the limits of compositions achievable by implanting ion species A into material B, or by implanting A^+ into material AB. The formation kinetics of the implanted surface layer was determined by both sputtering and atomic mixing effects. The model yielded results in good agreement with preliminary experimental results. (Chapter 5)

One of the important implications of sputter-induced surface layer composition changes has been their effects on the use of sputtering in surface-cleaning and in depth-profiling techniques. In this respect, we also studied the effect of atomic mixing and preferential sputtering on the evolution of very thin surface layers during sputter-etching. We observed that, for low ion doses, the atomic mixing effect first produced a uniformly alloyed surface layer with a thickness comparable to the ion range. Then, during the successive steps of sputter-etching, the surface layer maintained a constant thickness, but with a decreasing alloy (or impurity) concentration. Again, the previously developed model was extended for the present case. It also combined the results into a consistent picture. Based on these studies, we then extended the model further to predict the effect of atomic mixing and preferential

sputtering on the depth-profiling techniques. A simple equation was obtained, which related the "apparent" depth profiles to the true ones. (Chapter 6)

Finally, the effect of atomic mixing has been studied in the cases where the ion range penetrated through the interface between a surface metal film and an underlying Si-substrate. Silicide formation at the interface was observed for ion doses $\lesssim 10^{14} \text{ cm}^{-2}$. For higher doses, more Si-atoms were incorporated into the surface layer and the system appeared to be amorphized. After being thermally annealed, the samples showed formation of metastable phases which had not been reported previously. The present results suggest that the ion-induced atomic mixing effect has the potential of producing thin-film materials with any desirable compositions or with compositions and structures unachievable by conventional metallurgical means. (Chapter 7).

4. ION-BEAM-INDUCED MODIFICATIONS OF THIN FILM STRUCTURES AND FORMATION OF METASTABLE PHASES

by

Bor-Yeu Tsaur

California Institute of Technology

April, 1980

The influences of energetic ion bombardment on the composition and structure of thin film materials and the utilization of ion-beam-mixing techniques to produce compounds and alloys are reported in this thesis.

Motivated by recent experimental observations that ion

bombardment can induce alteration of atomic distributions in composite materials, a systematic study of ion-induced modification of interface profile and structure has been carried out. By bombarding through a thin transition-metal film deposited on a Si substrate, significant atomic mixing was observed near the metal-Si interface at dose levels of $\sim 10^{15} \text{ cm}^{-2}$. The atomic mixing led to the formation of well-defined silicide phases which are identical to those obtained by normal thermal treatment. A macroscopic model based on collision-cascade mixing and radiation-enhanced diffusion mechanisms was proposed to account for the ion-induced interface reaction. The mixing process and its products were found to be strongly influenced by the implantation conditions such as ion energy, mass, fluence and sample temperature, as well as by the intrinsic properties of target material such as thermal diffusivity and radiation stability. Ion-beam-mixing at higher ion doses ($\sim 10^{16} \text{ cm}^{-2}$) led to the formation of more Si-rich phases or disordered metal-Si layers which are difficult to form or, in some cases, inaccessible by normal thermal process. The phenomenon of ion-induced silicide formation is similar to that observed in thermal annealing except that the radiation stability of phase structure is important in determining whether a silicide phase is formed or a disordered metal-Si mixture is formed. (Chapter 2)

The ion-beam-mixing process was then utilized to investigate the production of nonequilibrium (or metastable) phases. A metastable silicide phase of a stoichiometry Pt_2Si_3 has been obtained by heat treating a Si-rich amorphous Pt-Si alloy layer produced by ion-beam-mixing of thin PtSi (or Pt) films on Si. The Pt_2Si_3 phase is absent

in the equilibrium phase diagram of Pt-Si and has not been reported before. X-ray diffraction analysis established the crystal structure of Pt_2Si_3 to be hexagonal with lattice parameters $a = 3.841 \text{ \AA}$, $c = 11.924 \text{ \AA}$ and with 10 atoms per unit cell. The metastable phase was found to exhibit a superconducting transition onset at about 4.2 K and to become completely superconductive at temperature below 3.6 K. For the first time, a compound of this structure was observed to be a superconductive material. The transformation behavior of the ion-induced amorphous Pt_2Si_3 alloy has been studied by using resistivity measurements. The amorphous to metastable crystalline transformation occurred at $\sim 400^\circ\text{C}$ as indicated by an abrupt decrease of resistivity. The metastable phase then gradually decomposed into an equilibrium PtSi and Si mixture at temperatures above 550°C . The kinetics of amorphous to crystalline transformation have been determined by isothermal treatment over the temperature interval $376\text{--}392^\circ\text{C}$. The results were interpreted in terms of a classical nucleation and growth mechanism with a t^4 (time) dependence and an apparent activation enthalpy of 4.69 eV (108 kcal/mole). The microstructure of the alloys at various stages of transformation were studied by transmission electron microscopy and diffraction. The results were found to correlate well to the phase transformation behavior observed by resistivity measurements. (Chapters 3 and 4)

To further investigate the production of metastable phases by ion-beam-mixing, experiments have been performed in the simple eutectic system of Au-Si. An amorphous alloy with a uniform composition Au-28 at. % Si ($\sim \text{Au}_5\text{Si}_2$) was formed by bombarding through a thin Au film on Si, a result distinctly different from that obtained in normal

thermal treatment. Upon thermal annealing, the amorphous phase transforms into a metastable crystalline phase at $\sim 100^{\circ}\text{C}$, which then gradually decomposes into an equilibrium Au and Si mixture at higher temperatures. The present observations were compared with those obtained previously by rapid quenching techniques. The comparison of metastable phase formation in the Pt-Si and Au-Si systems revealed a correlation between the existence of metastable phases and eutectic compositions, as well as the importance of sample temperature during implantation for direct observation of metastable phases. (Chapter 5)

As an extension of compound formation by ion-beam-mixing of a thin layer on a thick substrate, we investigated the mixing of thin deposited layers as a scheme for producing compounds or alloys of desirable compositions. Multiple-layered samples consisting of thin alternate layers of two elements were prepared by sequential vacuum deposition of the two components onto an inert substrate such as SiO_2 or Al_2O_3 . The relative thicknesses of the individual layers were adjusted such that the average film composition was equal to a fixed, predetermined value. Ion bombardment was then performed to homogenize the layers on an atomic scale. Formation of supersaturated Ag-Cu and Au-Co solid solutions over a wide range of composition has been achieved. Extensions of alloy solubility and formation of amorphous phases have been obtained in the almost completely immiscible systems of Ag-Ni and Cu-Ta, respectively. The present scheme may promise to be a new technique for producing metastable phases which are difficult to form or unattainable by conventional rapid quenching techniques. (Chapter 6)

Finally, we consider the possibility of using ion-beam-mixing techniques as an alternative approach to direct high dose implantation for material surface modification. Comparison between ion-beam-mixing and high dose implantation is made to demonstrate the "effectiveness" of ion-beam-mixing in incorporating Au or Ag in single crystal Cu substrates. A simple diffusion model for the evolution of ion-beam-mixing of a thin surface layer on a thick substrate was then proposed. The model predicts the influence of implantation conditions and material properties on the redistribution of the thin surface layers. From a practical point of view, the technique of introducing foreign species by ion-beam-mixing process exhibits many attractive advantages over direct implantation because of significantly lower ion doses required and the ability to use simple ion sources. (Chapter 7)

5. PART I CHANNELING STUDIES OF SILICON INTERFACES

PART II DIFFUSION BARRIER PROPERTIES OF TITANIUM NITRIDE

by

Woontong Nathan Cheung

California Institute of Technology

May, 1980

The channeling effect of MeV ions in crystalline materials has been applied to study the interfaces of metals, silicides and oxides with single-crystal Si substrates. The study was facilitated by the development of thin (1500-5000 Å) Si crystals which enabled channeled ions to probe the interfacial region without first traversing the metal or the silicide layers. These investigations revealed that

a reaction occurs between the silicon and as-deposited metal layers. For the Ni-Si system, about three monolayers of Ni penetrate into Si and occupy interstitial sites. An interfacial layer is also found between silicides and Si. In contrast, an abrupt interface is found between SiO_2 and Si.

With conventional channeling techniques, the ion beam traverses first the overlayer and then the Si substrate. A Si peak is observed in the energy spectrum and the area of the peak can be converted to Si atoms/cm² from known Rutherford scattering cross-sections. The Si peak corresponds to the first few monolayers of crystalline Si (the "surface peak"), the non-registered Si at the interface and the amount of Si in the silicide or oxide. From recent theoretical and experimental studies on surfaces, the surface peak contribution can be accurately predicted.

Using different overlayer thicknesses, the stoichiometry of silicides and oxides and the interfacial disordered Si can be determined. In the case of metal-Si interfaces, the interfacial reactivity can be monitored by measuring the amount of non-registered Si at the interface. However, the conventional channeling technique is applicable only when the multiple scattering of the incident beam by the overlayer is small (i.e. thin overlayers and low atomic number elements).

Additional information on the nature of the interfacial disordered Si can be obtained by the thin-crystal channeling technique which involves the use of thin ($< 1 \mu\text{m}$), self-supporting Si crystals. With the ions first traversing the Si thin crystal along a channeling direction, the channeled ions are steered away from the atomic rows.

At the interfacial region, the channeled ions only interact with the interfacial Si atoms which are displaced $\lambda^{\rho} \approx 0.7\text{\AA}$ laterally from the atomic rows. There is no contribution from the first few crystalline Si layers to the measured Si peak; as there is in the case of conventional channeling. The combination of both conventional and thin-crystal channeling techniques provides further information about the interfacial disorder because of the different sensitivities of the two techniques to lateral displacements. Thin-crystal channeling has also been used to locate the relative position of foreign atoms with respect to the Si lattice near the interfacial region. This technique requires angular scan experiments along various axial and planar channeling directions.

For metal-Si interfaces, channeling results show that an interfacial reaction is initiated at room temperature with as-deposited metal layers (Ni, Pd, Cr, V and Au); Ag is the only exception. With the Ni-Si system, the interfacial reaction can be greatly reduced by cooling the substrate to 170°K during Ni deposition and ion beam analysis. The temperature dependence of the interfacial reactivity emphasizes the kinetic nature of the metal-Si interfaces and the importance of interfacial studies at low temperatures for meaningful comparison with abrupt metal-semiconductor interface models. The amount of disordered interfacial Si is observed to be high for metals which are dominant diffusion species in silicide formation (e.g. Ni and Pd). A lattice location experiment on the Ni-Si interface shows that ~ 3 monolayers of Ni atoms are situated interstitially at the tetrahedral sites of crystalline Si. This observation supports the interstitial diffusion model which was proposed by Tu to explain

the low-temperature formation of silicides.

Interfaces between Si and Pd_2Si , Ni_2Si , NiSi or NiSi_2 have also been investigated by thin-crystal channeling. The Ni_2Si -Si interface shows $\sim 4 \times 10^{16}$ atoms/cm² of excess Si above an "ideal" Ni_2Si -Si interface. The other silicide-Si interfaces all show disordered interfacial Si of $< 8 \times 10^{15}$ atoms/cm². The amount of interfacial disorder correlates with the transformation temperature for the next stable silicide phase. For example, the Ni_2Si phase (which exhibits the highest interfacial disorder) transforms to NiSi at $\sim 350^\circ\text{C}$. In contrast, the other silicide phases, Pd_2Si and NiSi , require a much higher transformation temperature ($\sim 700^\circ\text{C}$).

The SiO_2 -Si interface has been studied by both conventional and thin-crystal channeling. The results show that thermally grown oxides on (110) Si are stoichiometric SiO_2 at least down to a thickness of 4 Å. By comparing the channeling data with predictions based on a various number of reconstructed Si layers, an abrupt SiO_2 -Si interface is deduced with 2 monolayers of the Si single crystal being reconstructed at the interface.

PART II

This part of the thesis is concerned with the deposition and evaluation of titanium nitride (TiN) layers as diffusion barriers in contact metallization on Si devices. The application of TiN to Si solar cell contacts (i.e., the TiN-Ti-Ag metallization scheme) has been demonstrated to withstand a 600°C , 10 min anneal without degrading the cell's performance.

Titanium nitride films have been prepared by reactive sputtering of Ti in a nitrogen plasma. The nitride films are identified by TEM and X-ray diffraction to have the NaCl structure with a lattice parameter of $4.24 \pm 0.02 \text{ \AA}$. Electrical properties and atomic composition of the films have been studied as a function of sputtering RF power (500 - 1500 W) and nitrogen pressure (3-100 mT). Backscattering analysis shows that the films have a composition close to stoichiometric TiN but with a slight tendency for higher nitrogen content. Oxygen is the major contaminant in the nitride films. The oxygen content strongly depends on the sputtering parameters and a high oxygen content corresponds to high electrical resistivity of the TiN films. The lowest resistivity ($\sim 170 \text{ }\mu\Omega\text{-cm}$) is obtained by sputtering with high RF power and low nitrogen pressure.

The effectiveness of titanium nitride films as a diffusion barrier between various metals and single-crystal Si substrate or Ti on single-crystal Si substrate is investigated by backscattering spectrometry, SEM and EDAX. The temperature range of interest is from 400°C to 700°C . Various metals of high electrical conductivity such as Au, Ag, Al, Cu and Pd are used as the top metal layer. By interposing a thin layer of TiN ($\sim 1000 \text{ \AA}$) between the metal and substrate, the failure temperature (i.e., the temperature at which metal-substrate inter-diffusion becomes significant) can be greatly increased. The failure temperature of the TiN layers as a diffusion barrier is related to the metal-silicon eutectic temperature. SEM studies show that the interdiffused layer is laterally non-uniform and is initiated at isolated spots across the sample's surface. It is believed that grain boundaries or pinholes in the TiN films are

the weak links in the diffusion barrier properties of TiN.

As an application for high-temperature diffusion barriers, the Ag-Ti-TiN metallization scheme has been tested on shallow-junction ($\sim 2000 \text{ \AA}$) Si solar cells. The conventional Ti-Pd-Ag metallization scheme has been shown to fail after a 600°C , 10 min anneal which is required for a glass encapsulation process. With the TiN-Ti-Ag scheme, no degradation of cell performance can be observed after the 600°C , 10 min anneal if the TiN layer is $\gtrsim 1500 \text{ \AA}$.

6. THE CHEMICAL STRUCTURE OF METAL/SEMICONDUCTOR INTERFACES AS DETERMINED BY X-RAY PHOTOELECTRON SPECTROSCOPY

by

Paula Jean Grunthaner

California Institute of Technology

May, 1980

The chemical nature of transition metal/silicon interfaces has been investigated using x-ray photoelectron (XPS) and Rutherford backscattering (RBS) spectrometry. In particular, the Ni/Ni₂Si, Si/Ni₂Si, and Ni/Si transitional regions have been examined in detail. The effect of oxygen impurities on the Ni/NiSi interface has been studied using ion implantation and $^{16}\text{O}(d,\alpha)^{14}\text{N}$ nuclear reactions in conjunction with XPS and RBS. Preliminary results on the Pd/Pd₂Si and Pt/Pt₂Si interfaces are presented and contrasted to the Ni system.

A technique for studying silicide/silicon and silicide/metal interfaces has been developed in the course of this work. The approach exploits the exponential attenuation of photoemission intensities to dynamically monitor the advancing planar silicide growth front during

the *in situ* growth of the silicide. The technique allows the examination of a realistic interface bounded on either side by an extended solid without the chemical and structural perturbations caused by conventional depth profiling methods. The local chemical environment of both the silicon and transition metal atoms has been established through analysis of the observed binding energy shifts in the photoemission spectra. $^4\text{He}^+$ backscattering has been used to follow the progression of the thin film reaction and to provide quantitative information on atomic composition.

These interfacial experiments demonstrated that the local environment of the Ni atoms at the Si/Ni₂Si interface is more Si-rich than that found for Ni in Ni₂Si. The transition layer is not a unique silicide phase, but rather is graded in composition. The first detectable Ni 2p_{3/2} signal is consistent with a single Ni atom located in the octahedral/tetrahedral interstitial voids in a pure Si lattice. The width of the amorphous Si/Ni₂Si interface was determined to be at least 1.5λ , where λ is the escape depth for Ni 2p electrons in the interfacial layer. A lower limit of 22 Å may be placed on the width of the transition region assuming a value of 15 Å for λ .

The Ni/Ni₂Si interface was examined using both amorphous and crystalline Si as a substrate. In each case, it was demonstrated that the Si atoms in the transition region are in a substantially more Ni-rich environment than that found for Si in Ni₂Si. These regions are again of graded composition. The first Si 2p signal observed is consistent with a metallic-like Si substituted in the fcc lattice of Ni metal. The essential difference between the Ni/Ni₂Si interface using a crystalline substrate as compared to an amorphous

substrate is that the former is 2 - 3 times narrower (0.6λ) than the latter (1.5λ).

The as-deposited Ni/Si interface was investigated by monitoring the evolution of the Ni and Si core levels as multiple monolayers of Ni were deposited on Si $\langle 100 \rangle$. The data indicate the presence of a chemically graded transition region which ranges in stoichiometry from Ni atoms bound in the Si interstitial voids on the $\langle 100 \rangle$ Si side of the interface to Si atoms substituted in the Ni metal lattice on the Ni^o side of the interface.

The chemical nature of the Ni/Si interface as a function of the substrate temperature was also examined. It was shown that substantial chemical interaction occurs between the Ni and Si substrate at temperatures as low as 100° K. Ni metal was deposited on an inert substrate to demonstrate that aggregation effects were not responsible for the observed chemical shifts.

The dependence of the Ni 2p binding energy on the substrate temperature also demonstrated that the initial Ni atom deposited on the Si surface must drop into the interstitial Si voids rather than being bound on the surface. The behavior of the Ni 2p binding energy as a function of Ni coverage at elevated substrate temperatures suggests the presence of several distinct Ni environments.

The effect of oxygen impurities on the Ni/Ni₂Si interface was investigated via ion implantation using XPS, RBS, and $^{16}\text{O}(d,\alpha)^{14}\text{N}$ nuclear reactions. It was shown that 2.2×10^{16} O/cm² are sufficient to block the diffusion of the Ni metal and thereby inhibit the silicide reaction. The data demonstrate that as the advancing Ni/Ni₂Si interface encounters oxygen in the Ni film, silicon suboxides are formed.

As more oxygen is encountered, SiO_2 is formed. When a sufficient layer of SiO_2 has formed, the Ni metal is no longer able to diffuse through to the $\text{Si/Ni}_2\text{Si}$ interface to continue the solid phase reaction.

Preliminary results for the $\text{Pd/Pd}_2\text{Si}$ and $\text{Pt/Pt}_2\text{Si}$ interfaces are presented and contrasted to those found for the $\text{Ni/Ni}_2\text{Si}$ system. The data suggest that, as the Ni case, the limiting environment for Si at the $\text{Pd/Pd}_2\text{Si}$ interface is metallic-like with a high ligancy. We propose this is a Si atom substituted in the fcc lattice of Pd metal. The Si atoms at the $\text{Pt/Pt}_2\text{Si}$ interface, on the other hand, rest in a site of substantially lower coordination number in the fcc Pt lattice. This is suggestive of an interstitial defect site.

Both the $\text{Pd/Pd}_2\text{Si}$ and $\text{Pt/Pt}_2\text{Si}$ interfaces are found to be graded in composition. Estimations of these widths indicate that the metal/silicon interface widths decrease in the order $\text{Ni} > \text{Pt} > \text{Pd}$.

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